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IX.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE, UNDER THE DIRECTION OF PROFESSOR J. P. COOKE.

DOUBLE HALOIDS OF ANTIMONY AND POTASSIUM.

By Francis Gano Benedict.

Presented February 14, 1894.

Of recent years an extended investigation of the nature and structure of the double haloids has been undertaken. The Rubidium and Cæsium compounds with antimonious chloride have received a good deal of attention, but an examination of the literature relative to this line of work shows marked variations in analyses as well as formulæ, ascribed to the several compounds resulting from the interaction of potassic chloride and antimonious chloride.

Accordingly an investigation was commenced to determine accurately the true nature of these salts, resulting in the preparation and analysis of four compounds.

The success of the research is greatly due to the direction and timely suggestions of Professor Cooke.

The first work that appears to have been done on these compounds is that of Jacquelaine* and Poggiale.†

In 1837 Jacquelaine ‡ described a salt formed by the union of $SbCl_3$ with 2 KCl as crystallizing in oblique rhombic prisms. His analysis is subjoined.

		Calculated.	Found.
Cl	1106.5	46.0	46.3
Sb	806.4	33.5	32.8
K	489.9	20.4	20.2
		99.9	99.3

In 1845 Poggiale § described two salts; i. e. one with 2 KCl or $SbCl_3 . 2 KCl$, and one with 3 KCl, or $SbCl_3 . 3 KCl$. The latter is described as deliquescent, turns yellow in the air, crystallizes in leaves, and is decomposed by water and heat. "L'eau mère abandonnée à une évaporation spontanée donne des hexaèdres composés de $SbCl_3 . 2\,KCl$."

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* Ann. Chim. Phys., LXVI 129.

† Comptes Rendus, XX. 1180.

‡ *Loc. cit.*

§ *Loc. cit.*

Thus confusion arises regarding the salt $SbCl_3 . 2\,KCl$, as Jacquelaine states the crystalline form to be an oblique rhombic prism, while Poggiale maintains that it is cubical.

Gmelin[*] states, "The aqueous solution of a mixture of two atoms of chloride of potassium and one atom of terchloride of antimony yields oblique rhombic prisms (Jacquelaine)." Jacquelaine's analysis is added. Formula $SbCl_3 . 2\,KCl$. "$SbCl_3 . 3\,KCl$ crystallizes in laminæ; deliquescent; decomposed by boiling water (Poggiale)."

Pelouze and Fremy[†] state that Sb_2Cl_3 forms many double chlorides with metals, especially alkaline chlorides. The general formula for these is $(MCl)_3Sb_2Cl_3$. Chloride of potassium forms, however, two salts, $(KCl)_3Sb_2Cl_3$ and $(KCl)_2Sb_2Cl_3$.

Watts's Dictionary[‡] states: "By mixing concentrated solutions of $SbCl_3$ and alkaline chlorides, and evaporating, double salts are formed, e. g.:

$3\,KCl . SbCl_3$, and $3\,KCl . SbBr_3$, etc."

Storer[§] mentions two salts:

(*a*) $2\,KCl . SbCl_3$, soluble in water without decomposition, more soluble than (*b*) in water (Jacquelaine).

(*b*) $3\,KCl . SbCl_3$, deliquescent, decomposed by hot water (Poggiale).

Graham-Otto[||] states that $SbCl_3$ forms double crystalline salts, with the chlorides of the alkaline and earthy alkaline metals.

Fehling[¶] mentions two salts:

(*a*) $3\,KCl . SbCl_3$, crystallizes in leaves, and is efflorescent.

(*b*) $2\,KCl . SbCl_3$, crystallizes in triclinic prisms.

Romanis[**] gives the specific gravity of a salt, to which he assigns the formula $SbCl_3 . 3\,KCl . 2\,H_2O$, as 2.42. But no method of its preparation or reference to previous work is given. This value is given in Clarke's table of specific gravities of double salts in the "Constants of Nature."

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[*] Handbook of Chemistry, Cavendish edition, Vol. IV. p. 381.

[†] Chemie General, Vol. III. p. 160.

[‡] Edition 1888, Vol. I. p. 287.

[§] Dictionary of Solubilities, p. 149.

[||] Michaelis edition, Vol. II. p. 555.

[¶] Neues Handwörterbuch der Chemie, ed. 1872, Vol. I. p. 670.

[**] Chemical News, XLIX 273.

Rammelsberg,* in 1855, gave the crystalline form of a salt, $SbCl_3 . 2 KCl$, as trimetric, and adds three measurements which he stated as extremely unreliable owing to the striations of the faces.

A summary of the crystallographic results obtained could be expressed as follows:

$SbCl_3 . 2 KCl$: — monoclinic, cubic, triclinic, trimetric.
$SbCl_3 . 3 KCl$: — crystallizes in leaves.

These variations warranted a research of these salts. Four compounds were obtained with the following composition:

$SbCl_3 . SbOCl . 2 KCl$ [Monoclinic].
$SbCl_3 . 2 KCl$ [Hexagonal].
$SbCl_3 . 2 KCl$ [Monoclinic].
$SbCl_3 . 2 KCl . 2 H_2O$ [Monoclinic].

METHODS OF ANALYSIS.

On inspection of the above formulæ it is evident that there must be a determination of each of the four elements, Antimony, Chlorine, Potassium, and Oxygen, together with one of water of crystallization.

Antimony determinations were made by dissolving the salt in tartaric acid solution, to which a small amount of hydrochloric acid was added. The antimonious sulphide resulting from the action of a solution of hydrogen sulphide on this solution was carefully washed and dried at 220°. The method was described in detail by Professor Cooke in his paper on the Revision of the Atomic Weight of Antimony.†

The *chlorine* determination consisted in weighing the silver chloride which had been precipitated from a solution of silver nitrate by a tartaric acid solution of the salt in question. The precipitate collected on a Gooch crucible was dried at 150°. In no case was there noticed any blackening due to presence of tartaric acid, even after heating to 235°.

Potassium Determination. — Several attempts were made to precipitate the potassium-platinic chloride, but the presence of tartaric acid, necessary for the solution of the salt, caused the formation of the insoluble potassic bitartrate, which interfered materially with the process.

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* Handbuch der Krystallographischen Chemie, p. 215.

† These Proceedings, XIII. 1-114.

The method next attempted was that described by Professor J. Lawrence Smith,* for the determination of alkalies in silicates. This consists essentially in rendering the antimony insoluble by fusion with pure calcic carbonate. Then in precipitating the dissolved calcic chloride by pure ammonic carbonate and igniting the evaporated filtrate till all ammonium salts are volatilized. This gave very close results. But later a method was employed which gave at once the total amount of potassic chloride as it existed in the salt. This consisted in igniting the weighed salt in a porcelain boat in a current of dry carbon dioxide till all the volatile matter ($SbCl_3$) was given off. The ignited mass was weighed and then dissolved in water, any insoluble portion being filtered and weighed. The difference in the two weights gives the amount of soluble matter which is potassic chloride.

Oxygen was estimated directly by weighing the insoluble portion of the residue from the ignition described under the head of potassium determination. This residue is Sb_2O_3. In Professor Cooke's paper previously referred to,† there is a description of the decomposition of $SbOCl$ to Sb_2O_3.

"Meanwhile we instituted a series of experiments with a view of studying the decomposition which the oxichloride of antimony undergoes under the action of heat, in the hope that we might thus discover some method by which the amount of oxichloride of antimony in our preparations might be directly determined. . . . It appeared that the decomposition took place in two stages. The first stage of the decomposition began between 167° and 175°, but was not completed until between 260° and 280°.

"The second stage began about 320°, but requires for its completion a red heat. During both stages the chloride of antimony sublimed, and there were left in the nacelle at the close of the process beautiful crystals of Sb_2O_3. In another experiment we used crystallized $Sb_4O_5Cl_2$ prepared in the same way as the SbOCl, but with different proportions of alcohol and chloride of antimony. In this case the decomposition did not begin until 320°, but in other respects both the process and the products were as in the first experiment. It was quite evident that the chemical changes which took place in the two stages of decomposition we have noticed were represented by the following reactions:

First stage, $5\,SbOCl = Sb_4O_5Cl_2 + SbCl_3;$ (1)

Second stage, $3\,Sb_4O_5Cl_2 = 5\,Sb_2O_3 + 2\,SbCl_3;$ (2)

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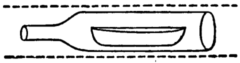
* Am. Journal of Science, Second Series, XV. 234, and XVI. 53.

† These Proceedings, XIII. 63, 64.

but the relative weights observed in the first two experiments were of no value, because it was evident that a no inconsiderable amount of Sb_2O_3 was lost by sublimation. Since, however, the small sublimate of oxide condensed in the glass combustion tube very much nearer the nacelle than the very much larger sublimate of chloride, we varied the apparatus in our third experiment so far as to place the nacelle in a tube of the shape represented in the accompanying figure.



"This tube was weighed with the nacelle, and was so selected that it quite closely fitted the combustion tube within which it was placed for heating, as shown in the figure by dotted lines. And it is evident that, while with this arrangement the $SbCl_3$ would be swept by the CO_2 gas into the colder portion of the combustion tube, the greater part at least of the sublimed oxide would be retained in the small tube, which was of course at each stage weighed with the nacelle as at first. . . . It was evident from this determination that the order of the decomposition was precisely that indicated by our reactions."

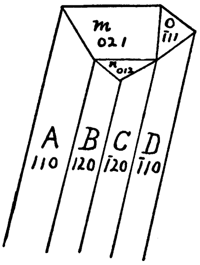
In these experiments with the double haloids very little of the Sb_2O_3 was volatilized, but proceeding in the described manner the exact amount of resulting Sb_2O_3 could be found, from which was readily calculated the per cent of oxygen.

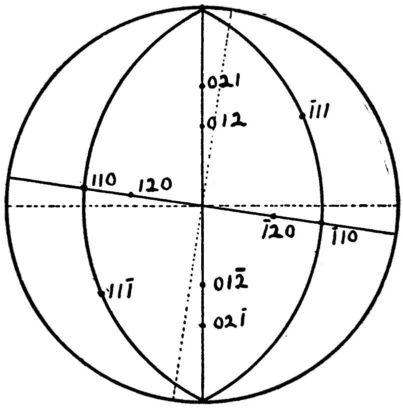
The determinations of *water of crystallization* were made in the usual way by heating in an air bath a weighed quantity of salt to constant weight at a temperature of 100–105°. This will be described more fully later.

Method of Complete Analysis.— Obviously the ignition of the salt in a current of dry carbon-dioxide affords a means of determining the total amount of each element. The salt, dried at 100°, is weighed and placed in the porcelain boat with the covering as described. Upon ignition the $SbCl_3$ volatilizes, some Sb_2O_3 also volatilizes, but is condensed on the covering tube. There is left as a residue from ignition a mixture of KCl and Sb_2O_3 (if any combined oxygen is present in the salt). Hence we see that the data are sufficient to give the exact weight of $SbCl_3$, Sb_2O_3, and KCl, from which can be calculated the total Sb, Cl, K, and O. This method, after abundant proof of its correctness, obtained by comparing the percentages of Sb and Cl resulting from ignition with the direct determination of the total Sb and Cl, was applied in all the later determinations for the estimation of potassium and oxygen. The calculated percentage of Cl and Sb from the data given were, however, invariably corroborated by an estimation of the total Sb and Cl.

The crystalline form of each salt is represented by the free hand sketches, and the accompanying stereographic projections show more accurately the mathematical relation of the planes.

$SbCl_3 . SbOCl . 2 KCl$ [Monoclinic].





$$a : b : c = 1 : 1.913 : .9877.$$

$$\beta = 81° \ 4'.$$

Angles between Normals.

A B	m n
$110 \wedge 120 = 20° \ 45'$	$021 \wedge 012 = 18° \ 40'$
B C	m m′
$120 \wedge \bar{1}20 = 85° \ 30'$	$021 \wedge 0\bar{2}1 = 54° \ 35'$
C D	O D
$\bar{1}20 \wedge \bar{1}10 = 20° \ 45'$	$\bar{1}11 \wedge \bar{1}10 = 46° \ 6'$
A A′	O O′
$110 \wedge 1\bar{1}0 = 54° \ 30'$	$\bar{1}11 \wedge \bar{1}\bar{1}1 = 44° \ 0'$

These crystals were quite permanent in the air, presented no difficulty in manipulation, and allowed very close measurements with the reflecting goniometer.

The salt is decomposed immediately by hot or cold water; insoluble in hot or cold saturated solution of potassic chloride, hot or cold bisulphide of carbon, alcohol, or ligroin; soluble in hot glacial acetic acid, but on cooling a heavy white precipitate of oxichloride of antimony settles out. It is readily soluble in hydrochloric acid and a solution of tartaric acid. It will crystallize from a solution containing free hydrochloric acid. Since a determination of antimony and chlorine gave results which showed an exact ratio of one of antimony to three of chlorine, it was obvious that there must be something combined with the potassium in the salt. A determination of potassium by Smith's method left about three per cent of the salt to be accounted for. The use of dried salt eliminated water from the list of probable constituents, and chemically pure materials guarded against impurities. The fact that Professor Cooke invariably found a certain amount of oxichloride of antimony in the chloride led to a search for oxygen (combined) as the fourth element after the described method. Obviously heating the salt would drive off all the antimonious chloride, and whatever oxygen there was present was combined as the oxichloride, which upon heat left a residue of Sb_2O_3. Calculating the per cent of oxygen from the weighed Sb_2O_3 gave the required per cent. After a few preliminary experiments were tried, a series of ignitions were carefully made, with the following results.

Columns I., III., and V. contain the direct percentages of each element according to the total estimation.

I. Sb.	II.	III. Cl.	IV.	V. K.	VI.	VII. O.
Sb. Total Determination.	Sb. Calc. from Ignition.	Cl. Total Determination.	Cl. Calc. from Ignition.	K. Smith's Method.	K. Calc. from Ignition.	O. Calc. from Sb_2O_3.
43.78	43.58	39.17	38.70	14.43	14.31	2.92
44.05	43.78	39.11	38.89	14.61	14.26	2.94
*43.40	43.87	39.03	†38.58	—	14.17	2.93
43.67	44.07	39.11	38.89	—	14.50	3.04
43.62	—	38.94	—	—	14.60	—
43.69	—	—	—	—	14.60	—
43.70	43.85	39.07	38.76	14.52	14.40	2.96
43.78		**38.91**		**14.46**		**2.96**

* Probably some undecomposed oxichloride.

† This sample was undoubtedly heated too high when drying.

An examination of the above two sets of averages establishes beyond a doubt the value of the ignition method of analysis in these compounds. With these data the formula nearest approaching their values is $SbCl_3 . SbOCl . 2 KCl$.

	Calculated* for $SbCl_3$, SbOCl, 2 KCl.	Found.
Sb	43.88	43.78
Cl	38.89	38.91
K	14.31	14.46
O	2.92	2.96
	100.00	100.11

It is evident, therefore, that this salt has the formula

$$SbCl_3 . SbOCl . 2 KCl.$$

$SbCl_3$. 2 KCl [Hexagonal].

These crystals are tabular, consisting of a regular hexagonal prism terminated by basal planes.

With the polarizing microscope it gives a very perfect uniaxial figure of a positive sign. In this figure the yellow ring is the innermost, therefore $\rho < \nu$.

It being quite permanent in the air, no difficulty was experienced in making the above examinations. Hot or cold water immediately decomposes it. It is soluble in a solution of tartaric acid, and also readily soluble in dilute hydrochloric acid, from which it can be crystallized.

The antimony and chlorine were determined by precipitation, and the potassium was weighed as potassic chloride after ignition in a current of dry carbon dioxide gas. In this residue there was not a trace of any insoluble matter (absence of Sb_2O_3) after ignition.

Here, all the $SbCl_3$ was volatilized, giving again the data for the calculation of the percentage composition.

	Calculated for $SbCl_3$, 2 KCl.	Found.
Sb	31.95	30.44
Cl	47.20	47.21
K	20.85	22.34
	100.00	99.99

The loss of 1.51% in antimony and the gain of 1.49% in potassium were at first difficult to explain, but on taking into consideration the fact that the per cent of chlorine in $SbCl_3$ is 47.04, in KCl is 47.53, and in this salt is 47.20, it is evident that an excess of potassic chloride would explain the discrepancy from the calculated results, and not materially interfere with the per cent of chlorine.

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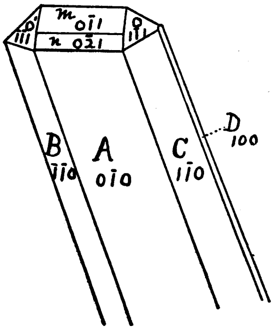
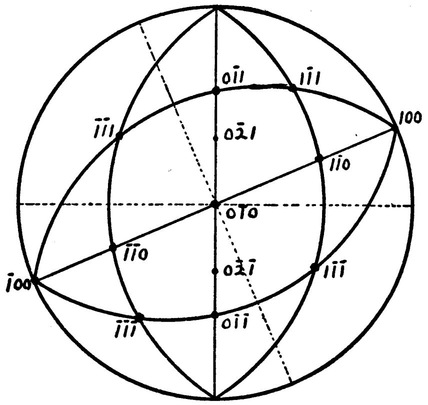
* Atomic weights used: — Sb 120; Cl 35.456; K 39.14; O 16.

The crystals of this salt are, as has been stated, hexagonal plates. These plates pile up in layers, leaving the prism faces very much striated. This process of formation would tend to the occlusion of mother liquor rich in potassic chloride. As a matter of fact, a microscopical examination of the smallest, clearest, and most perfect crystals revealed numberless cavities with air bubbles and bubbles of liquid. This was the only salt in which such cavities and bubbles were found.

$SbCl_3 . 2\,KCl$ [Monoclinic].





$a : b : c = 1 : 1.381 : .9974.$

$\beta = 68^\circ\ 57'.$

Angles between Normals.

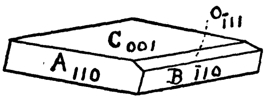
A B	A *n*
$0\bar{1}0 \wedge \bar{1}\bar{1}0 = 56^\circ\ 6'$	$0\bar{1}0 \wedge 0\bar{2}1 = 36^\circ\ 45'$
A C	A *m*
$0\bar{1}0 \wedge 1\bar{1}0 = 56^\circ\ 0'$	$0\bar{1}0 \wedge 0\bar{1}1 = 56^\circ\ 0'$
C D	*m* *m*′
$1\bar{1}0 \wedge 100 = 34^\circ\ 0'$	$0\bar{1}1 \wedge 011 = 68^\circ\ 0'$
C C′	C *m*
$1\bar{1}0 \wedge 110 = 68^\circ\ 3'$	$1\bar{1}0 \wedge 0\bar{1}1 = 56^\circ\ 0'$
O′ O″	B O′
$\bar{1}\bar{1}1 \wedge \bar{1}11 = 61^\circ\ 20'$	$\bar{1}\bar{1}0 \wedge \bar{1}\bar{1}1 = 46^\circ\ 15'$

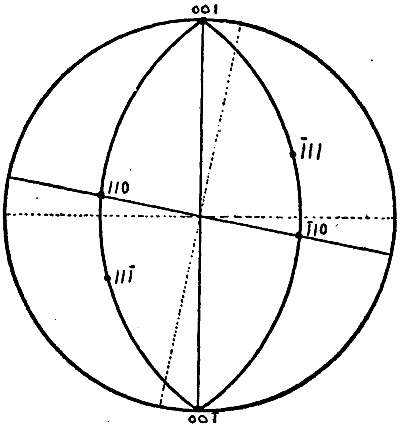
This salt is quite stable in the air. It is the dimorphous form of the previous salt.

	Calculated for $SbCl_3 . 2 KCl$.	Found.
Sb	31.95	32.13
Cl	47.20	47.20
K	20.85	20.70
	100.00	100.03

Here there is no great difference between the antimony and potassium percentages as before. Microscopic examination showed no cavities or bubbles of enclosed liquid.

$SbCl_3 . 2 KCl . 2 H_2O$ [Monoclinic].





$$a : b : c = 1 : 1.3798 : .9358.$$
$$\beta = 78° 30'.$$

Angles between Normals.

A B
$110 \wedge \bar{1}10 = 111° 40'$

A A'
$110 \wedge 1\bar{1}0 = 68° 48'$

A C
$110 \wedge 001 = 80° 35'$

A' C
$1\bar{1}0 \wedge 001 = 80° 28'$

B C
$\bar{1}10 \wedge 001 = 99° 30'$

B' C
$\bar{1}\bar{1}0 \wedge 001 = 99° 28'$

B B'
$\bar{1}10 \wedge \bar{1}\bar{1}0 = 68° 42'$

B O
$\bar{1}10 \wedge \bar{1}11 = 34° 31'$

O C
$\bar{1}11 \wedge 001 = 64° 57'$

The fact that this salt effloresced so readily at first prevented the making of any accurate crystallographic measurements. However, it was found that at a temperature of about —5° the salt retained its lustre for a sufficient length of time to afford very accurate measurements and crystallographic study. These crystals were of a tabular form, and upon looking through the plate with a polarizing microscope no interference figure could be discerned.

As the formula indicates, this is a hydrate of the two previous salts.

The water of crystallization is easily lost, even at a temperature of 15°. The weather at this period of the investigation was extremely cold, in consequence of which it was found that when the salt is kept in a room with the temperature at about —5°, it retains its water of crystallization for a period long enough to admit of weighing. The salt in the form of large isolated crystals was taken from the mother liquor, hastily dried between sheets of filter paper, crushed in a mortar, and finally rubbed between filter papers. Then it was transferred to a glass-stoppered weighing bottle, the whole operation occupying not more than 80 seconds at a temperature of —5°. From the weighing bottle it was quickly removed as desired; — the loss in weight of the bottle showing the amount of salt used. The determination of the water of crystallization presented several difficulties. Heating the salt in an air bath at 90°–95°, it will not come to constant weight in ten hours. If heated to 110°, it continues to lose in weight for a long time; in fact, there is a decomposition accompanied by the liberation of chlorine. Analysis of the salt heated to 95° showed that no Cl had gone off, but when heated to 110° there was a marked diminution of the percentage of chlorine, indicating a decomposition. At a temperature of 104° the salt will lose weight rapidly for a while, and then lose it *very* slowly for hours. Evidently the point where the last portion of water goes off and the point where the chlorine begins to be given off are nearly coincident. A great many determinations were made, and by estimating the chlorine every time the point could be very closely determined. Almost all the water will be given off in a desiccator over sulphuric acid, but it is a long time before the last trace is gone (thirty hours).

1. In a desiccator after 30 hours, the per cent of H_2O = 8.743
2. Heated in air bath 90–95°, at end of 4 hours = 8.476
3. " " 140° for 1 hour = 9.874
4. " " 105–107° for 5 hours = 10.24
5. " " 100–105° " " = 8.765

Nos. 1 and 5. The water has all been given off, and these are the two best values for the per cent of water. No. 2. The water is not all off yet, as shown by heating another hour, when per cent = 8.62. Nos. 3 and 4 both showed by analysis that chlorine had been evolved. The dried salts from Nos. 1 and 5 were used in the ignitions, and these gave results corresponding to the formula $SbCl_3 . 2 KCl$. Calculating the percentages for the additional water of crystallization, the following result was obtained: —

	Calculated for $SbCl_3 . 2 KCl . 2 H_2O$.	Found.
Sb	29.16	29.07
Cl	43.07	43.07
K	19.02	18.53
H_2O	8.75	8.76
	100.00	99.43

In the ignited residue there was no insoluble portion of Sb_2O_3. The evidence warrants the selection of $SbCl_3 . 2 KCl . 2 H_2O$ as the formula for this salt.

The conditions under which these salts form are closely related. So much so that it has been difficult to establish the exact conditions under which each salt may be isolated. At first the work was wholly tentative, using a saturated solution of potassic chloride, and adding crystallized antimonious chloride, filtering off any insoluble portion. In this way were obtained the salts $SbCl_3 . SbOCl . 2 KCl$, and $SbCl_3 . 2 KCl$ (hexagonal). But in order more closely to study the relations of each to the others, a series of experiments was carried out in watch glasses.

To about 5 c. c. of a saturated solution of potassic chloride were added 5 grams of crystallized antimonious chloride; when this had all dissolved, as it will in the cold, more $SbCl_3$ was added, till the solution was so to speak saturated with $SbCl_3$. In all, about 30 grams of $SbCl_3$ were added. In each of a series of watch glasses was placed 1 c. c. of the above solution, and to the several glasses increasing amounts of a saturated solution of potassic chloride were added,— from 1 c. c. in the first to 5 c. c. in the last. In each a white precipitate was formed which redissolved on heating.

Then the reverse was tried, i. e. 2 c. c. $SbCl_3$, 1 c. c. KCl, down to 5 c. c. $SbCl_3$, 1 c. c. KCl. There was a precipitate in each watch glass, which however dissolved on heating. The watch glasses were placed on the window sill, with moderately cold weather, and examined at intervals.

Designating the salts by Roman numerals : —

$SbCl_3 . SbOCl . 2\ KCl$ . . . . I.
$SbCl_3 . 2\ KCl$ [hexagonal] . . . . II.
$SbCl_3 . 2\ KCl . 2\ H_2O$ . . . . III.

Contents of Watch Glass. Nov. 11, A. M.	Nov. 11, P. M.	Nov. 13, 8.30 A. M.	Nov. 13, 4 P. M. (Colder.)	Nov. 14, 6 P. M.
1 c.c. $SbCl_3$ sol. 1 c.c. KCl "	Monoclinic prisms. I.	Same. I.	Same. I.	Same. I.
1 c.c. $SbCl_3$ sol. 2 c.c. KCl "	I.	I.	General mass I., but the edges rounded off. A few II. Indications of III.	A few II. Two crystals of III.
1 c.c. $SbCl_3$ sol. 3 c.c. KCl "	I.	I.	I. a few remain. II. predominates. III. a good crystal.	Chiefly II. Several III. Remains of a few I.
1 c.c. $SbCl_3$ sol. 4 c.c. KCl "	I.	I.	Chiefly cubo-octahedrons of potassic chloride. II. present. I. but few remain.	Chiefly II. with amorphous KCl.
1 c.c. $SbCl_3$ sol. 5 c.c. KCl "	Clouds up. Possible indications of I.	Precipitate at bottom a few I. floating.	Chiefly cubo-octahedrons of KCl. No signs of I. A very few II.	Chiefly cubo-octahedrons with a few II.
2 c.c. $SbCl_3$ sol. 1 c.c. KCl "	—	—	Scum of white oxichloride.	Same.
down to 5 c.c. $SbCl_3$ " 1 c.c. KCl "	—	—	—	—

During these experiments a number of mixtures of the two salts were crystallized in dishes under varying conditions.

Regarding salt I. ($SbCl_3 . SbOCl . 2\ KCl$), the evidence indicated that it crystallizes best from solutions by spontaneous evaporation in a cool place. Solutions should be preferably not too concentrated, and contain no large amount of free acid, i. e. no acid used in assisting the solution.

The hexagonal salt II. ($SbCl_3 . 2\ KCl$) results by evaporating either by heat or a vacuum desiccator a solution of almost any proportion of $SbCl_3$ and KCl with or without free acid; preferably concentrated solutions. This salt is the one most readily obtained of all the salts.

The hydrated salt III. ($SbCl_3 . 2\,KCl . 2\,H_2O$) crystallizes from moderately dilute solutions by exposure to severe cold, —10°. The presence of free hydrochloric acid does not interfere in any way, and possibly assists in the crystallization, provided it is not in too great an excess.

Lastly, *the monoclinic form of* $SbCl_3 . 2\,KCl$. The hexagonal salt is readily obtained, and, if it is left in the mother liquor, after a few days undergoes a transformation from the hexagonal to the monoclinic. This is apparently accomplished by the building up of the hexagonal plates into a dumb-bell form, after which the planes of the monoclinic form are assumed, accompanied by an entire reconstruction of the crystal.

The mutual relations of these salts require further consideration. If a solution is made up as directed for preparing salt I. ($SbCl_3 . SbOCl . 2\,KCl$), the addition of one drop of water beyond a certain point will cause a white precipitate, which is soluble upon heating, but which *reappears* on cooling. If, however, a crop of I. crystals is taken from the solution, and the mother liquor be divided in two portions, water can be added to one of them in considerable quantity, till finally one drop produces a cloudiness, which disappears on heating, but reappears on cooling. If now the second half of the mother liquor be added to the dish, the precipitate will not redissolve in the cold, but on heating it goes completely into solution, and is not thrown out on cooling. If this solution was left to evaporate after removing the crystals of I., there would soon be a deposit of II. ($SbCl_3 . 2\,KCl$, hexagonal). But it is found that the addition of water as above described will promote the crystallization of more I. ($SbCl_3 . SbOCl . 2\,KCl$).

When a solution depositing I. is placed at a temperature of —5°, then III. will immediately be deposited.

When the salt I. is dissolved in hydrochloric acid just strong enough to effect the solution, there is deposited chiefly II., together with a few I.

When the salt II. is dissolved under the same conditions, there is dissociation, and the potassic chloride crystallizes out as cubes or cubo-octahedrons at first. Later, the salt will crystallize out itself as II.

As has been before stated, II. hexagonal goes into II. monoclinic on long standing at a moderate temperature. Considerable difficulty was experienced in attempting these crystallizations during rainy weather. The excessive moisture caused a white scum of oxichloride on every receptacle of the various solutions.

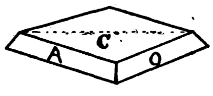
According to all analogy regarding the constitution of double salts, there would be three possible forms for the double chlorides of antimony and potassium ; i. e. $SbCl_3 . KCl$; $SbCl_3 . 2\,KCl$; $SbCl_3 . 3\,KCl$. Singularly enough, as yet only the second one is obtained, and that is dimorphous. Solutions were made containing molecular proportions for $SbCl_3 . KCl$ and $SbCl_3 . 3\,KCl$. Each solution was divided into two parts, one of which was acidulated with hydrochloric acid, and the other not. The only resulting salts were:

1st solution, i. e. $SbCl_3 . KCl = $ I. and II.
2d " " $SbCl_3 . 3\,KCl = $ at first a lot of cubo-octahedrons of potassic chloride; later, II.

Although so many different forms were mentioned by previous writers, none such have been definitely proven in this research. Regarding the statement of Poggiale,* that the $SbCl_3 . 2\,KCl$ crystallizes in cubes, it may be mentioned that in the preparation of that salt a number of crystals appeared under the microscope as perfect cubes. But on isolating them and nursing them till they were of sufficient size to admit measurement, they were proven to be the hydrated salt III. ($SbCl_3 . 2\,KCl . 2\,H_2O$), with the angle not 90° but 80°. It is simply a different habit of the tabular crystal with no octahedral face. It may be possible that he observed the cubes of potassic chloride, which will crystallize from many of these solutions.

The mention of a triclinic crystal by Fehling * can be accounted for by the peculiar habit of this same salt III. of developing more rapidly on one side than another, giving to the eye a decidedly triclinic appearance. The trimetric form of Rammelsberg † may be explained in two ways.

First, the salt III. crystallizes often as per diagram, in which the plane of symmetry is through the dotted line, and O represents the octahedral face,‡ but the lower face is wanting where the crystal rests on the dish. At first sight this was taken for a trimetric crystal, but the angle of $A \wedge C$ is different from that of $O \wedge C$, and no interference figure is seen with the polarizing microscope.



Secondly, the salt ($SbCl_3 . 2\,KCl$, monoclinic) crystallizes in diamond-shaped tablets, but the plane of symmetry is parallel to A, and octahedral faces are all wanting.* This occurs when there is a thin layer of mother liquor in the crystallizing dish. Obviously, this would be taken at first sight for trimetric, but measurement of angles and stauroscopic observations indisputably prove otherwise.

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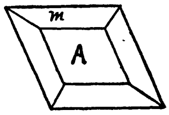
* This paper, page 213. † Ibid., page 214. ‡ Ibid., page 221.



No crystals were obtained crystallizing in any manner like leaves. In some cases there was obtained, when an exceedingly thin layer of liquid was allowed to evaporate, an arborescent formation as a thin coating on the bottom of the dish. This was $SbCl_3 . 2 KCl$.

The salt Jacquelaine † described as in oblique rhombic prisms, with a formula $SbCl_3 . 2 KCl$, may have been the salt described here as the monoclinic form of II., but it is rather singular that he made no mention of the hexagonal form which is the first to be obtained. On the other hand, it is quite possible that he meant the monoclinic salt, $SbCl_3 . SbOCl . 2 KCl$, which is the first to crystallize from molecular solutions of $SbCl_3 . 2 KCl$.

The writer is engaged in an investigation of the double salts of antimonious chloride with the bivalent metals.

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* This paper, page 220.

† Ibid., page 212.